PB83-168047

Trace Elements - Methodology, and Legislation

(U.S.) Environmental Monitoring and Support Lab.-Cincinnati, OH

1983

U.S. Department of Commerce
National Technical Information Service
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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before compl

1. REPORT NO.	2.	3
EPA-600/J-83-003	JOURNAL ARTICLE	PB83-168047

4. TITLE AND SUBTITLE	5. REPORT DATE
JOURNAL ARTICLE: Trace Elements--Methodology, and Legislation	1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
John F. Kopp and Theodore D. Martin	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Monitoring and Support Laboratory U. S. Environmental Protection Agency 26 W. St. Clair Street Cincinnati, Ohio 45268	10. PROGRAM ELEMENT NO. APB1A/BNC1A 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency 26 W. St. Clair Street Cincinnati, Ohio 45268	13. TYPE OF REPORT AND PERIOD COVERED Review article 14. SPONSORING AGENCY CODE EPA 600/06

15. SUPPLEMENTARY NOTES

REF: ASTM Standardization News, February 1983, pp. 18-21

16. ABSTRACT

This article has been requested by ASTM to be included in a special issue of Standardization News, dealing with analytical chemistry. The article traces federal water legislation as it pertains to drinking water and wastewater and how it applies to the approved methodology for metal analyses. Emission spectroscopy, atomic absorption, and inductively coupled argon plasma spectroscopy are discussed. A comparison of analytical detection limits, optimum ranges and advantages, as well as disadvantages, are discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
RELEASE TO PUBLIC	UNCLASSIFIED	5
	20. SECURITY CLASS *(This page)*	22. PRICE
	UNCLASSIFIED	

EPA Form 2220-1 (9-73)

EPA-600/J-33-003
JOURNAL ARTICLE

Trace Elements—Methodology, and Legislation

John F. Kopp
and
Theodore D. Martin

Trace element contaminants in water have long been of interest to the researcher and the health scientist, both from a physiological and a toxicological point of view. Various federal laws have been enacted over the years to limit the concentration of trace elements in public water supplies and in waste effluents discharged in the nation's waterways. Federal water legislation in the United States actually dates back to the 19th century when Congress enacted the River and Harbor Act of 1886. Federal standards for drinking water were first issued in 1914 to prevent the interstate spread of communicable diseases.

Although the Federal Water Pollution Control Act came into being in 1948, it was not until 1955 that a Presidential Advisory Committee on water resources policy recognized a strong need for more information on what was happening to the quality of the nation's water. Their recommendation was for an expanded program of basic data collection and evaluation. In the following year, the 84th Congress incorporated these recommendations into the Federal Water Pollution Control Act by providing for a federal-state-and local cooperative program to collect and disseminate basic data on water pollution and its prevention. Thus it was that the National Water Quality Network (NWQN) came into being with approximately 50 sampling sites located on various streams, rivers, and lakes of the United States. The first published results of these analyses appeared in late 1958, and included data on chemical measurements, radioactivity, plankton, and bacteriological measurements.[1] In subsequent years, trace elements were included in the analytical scheme.

TABLE 1—Typical Rotating Disc Spectrochemical Detection Limits, * μg/L

Zinc	20
Cadmium	20
Arsenic	100
Boron	10
Iron	10
Molybdenum	40
Manganese	10
Aluminum	40
Beryllium	0.1
Copper	10
Silver	2
Nickel	20
Cobalt	20
Lead	40
Chromium	10
Vanadium	40
Barium	2
Strontium	4

* In a water having a total dissolved solids content of 40 mg/L.

When the Environmental Protection Agency (EPA) was established in 1970, it assumed responsibility for setting and enforcing federal water regulations. In 1972, amendments to the Federal Water Pollution Control Act were enacted, that changed the thrust of enforcement from water quality standards regulating the amount of pollutants in a given body of water, to effluent limitations regulating the amount of pollutants being discharged from particular point sources.[2] Implementation of these amendments requires monitoring data on a variety of pollutants in all waste discharges. The list of pollutants includes a wide spectrum of both organic and inorganic analytes as well as a number of physical measurements. Section 304(h) of the Act required that the administrator of the EPA promulgate guidelines establishing test procedures for the analysis of these pollu-

[1] *National Water Quality Network, Annual Compilation of Data*, October 1, 1957—September 30, 1958. U.S. Department of Health, Education and Welfare, USPHS Publication No. 663, 1958.

[2] (86 Stat. 816, et seq. Public Law 92-500 (1972))

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tants. Such test procedures are to be used by permit applicants to demonstrate that effluent discharges meet applicable pollutant discharge limitations, and by the states and other enforcement agencies in routine or random monitoring of effluents to verify effectiveness of pollution control measures.

These guidelines require that analyses be performed by approved test procedures. The criteria for approval are that the test method should:

- Measure the desired constituent in the presence of interferences normally encountered, with precision and accuracy sufficient to meet the data needs;
- Utilize the equipment and skills normally available in the average water laboratory;
- Be in use in many laboratories or have been sufficiently tested to establish validity; and
- Be sufficiently rapid to permit routine use for the examination of large numbers of samples.

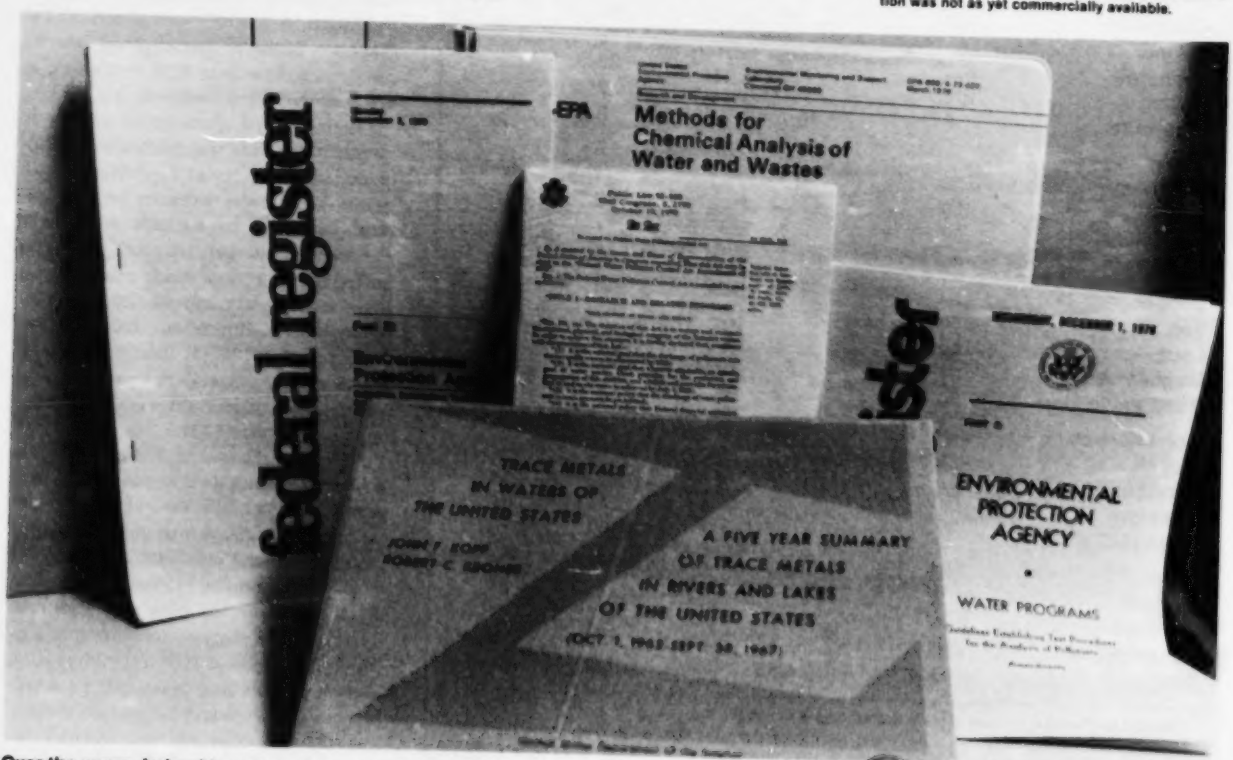
The 304(h) test procedures were originally proposed in the *Federal Register* of June 29, 1973, and promulgated on October 16, 1973.[3,4] Amendments followed on December 1, 1976 and December 3, 1979. The latter have yet to be promulgated.

In 1974, the Safe Drinking Water Act (SDWA) was enacted to assure that water supply systems serving the public meet minimum national standards.[5] The National Interim Primary Drinking Water Regulations (NIPDWR) promulgated on Dec. 24, 1975, also prescribed certain methods and/or techniques to determine compliance with the maximum contaminant levels.[6] Their criteria were similar to those used for approval of 304(h) test methods.

Prior to the 1972 amendments to the Federal Water Pollution Control Act, there were no requirements as to the analytical method used. For trace element analyses of the NWQN samples, a direct reading emission spectrometer was used. Nineteen elements were included in the spectrochemical program. The total procedure consisted of evaporating a specific volume of water to some lesser volume depending on the dissolved solids present. The concentrate was subsequently subjected to spectrochemical analysis using the rotating disc with high voltage spark excitation. In 1964, a five year summary of trace metal data in waters of the United States was published which, at that time, was perhaps the most comprehensive listing of its kind.[7] The procedure was described at the Pittsburgh Conference of 1964, and published in *Applied Spectroscopy* in 1965.[8]

Although the spectrochemical procedure was itself rapid, sample processing could be time-consuming. For waters low in dissolved solids, as much as a liter was concentrated to 2 mL, to arrive at a concentrate containing 20,000 mg solids/L. While a liter volume provided for good

[3] *Federal Register* (38 FR, 17318) 40 CFR 130 (June 29, 1973).
[4] *Federal Register* (38 FR, 28758) 40 CFR 136 (Oct. 18, 1973).
[5] Safe Drinking Water Act (Public Law 93-523) 1974.
[6] Federal Register (40 FR, 59566) 40 CFR 141 (Dec. 24, 1975).
[7] "Trace Metals in Waters of the United States—A Five Year Summary of Trace Metals in Rivers and Lakes of the United States." J. F. Kopp and R. C. Kroner, U.S. Department of the Interior, Federal Water Pollution Control Administration, Division of Pollution Surveillance, Cincinnati, OH (1964).
[8] The inductively coupled plasma (ICP) instrumentation was not as yet commercially available.


federal register
EPA
Methods for Chemical Analysis of Water and Wastes
TRACE METALS IN WATERS OF THE UNITED STATES
A FIVE YEAR SUMMARY OF TRACE METALS IN RIVERS AND LAKES OF THE UNITED STATES
ENVIRONMENTAL PROTECTION AGENCY
WATER PROGRAMS

Over the years, federal laws have been enacted to limit the concentration of trace elements in public water supplies and in waste effluents discharged in the nation's waterways.

sensitivity, the sample processing time required several hours of slow evaporation. A listing of typical detection limits achieved is shown in Table 1.

As interest in the occurrence of trace elements and cost-effective analytical techniques increased, the spectrochemical procedure was published by ASTM in Part 31 of the *Annual Book of ASTM Standards* as a proposed method both in 1977 and 1978. The technique never achieved standard designation, however, due to a lack of sufficient round-robin participants. Lack of interest in the technique was attributed to the fact that few water laboratories included direct reading spectrometers in their capabilities, and at the time there were no legal requirements for monitoring trace elements routinely.

Considering the 304(h) criteria described earlier and the absence of spectrometers in water laboratories, it is not surprising that atomic absorption (AA) became the approved technique for trace element analysis.[9] Although usually limited to a single elemental measurement per sample aspiration, AA was generally sufficiently sensitive and cost-effective. Guidelines for proper use of AA were originally published by ASTM as a tentative method in 1967 and elevated to standard in 1970. With the inclusion of the technique in many of the individual element standards, the general practice was dropped as a separate standard in 1981.

[9] "A Direct Reading Spectrochemical Procedure for the Measurement of Nineteen Minor Elements in Natural Water," *Applied Spectroscopy*, 19, 155 (1965).

TABLE 2—A Comparison of Estimated Instrumental Detection Limits, Atomic Absorption Versus Inductively Coupled Plasma Spectroscopy, μg/L

Element	Atomic Absorption[1] Direct Apiration	Atomic Absorption[1] Graphite Furnace	Inductively Coupled Argon Plasma[2]
Aluminum	100	3	45
Arsenic		1	53
Antimony	200	3	32
Barium	100	2	2
Beryllium	5	0.2	0.3
Boron			5
Cadmium	5	0.1	4
Calcium	10		10
Chromium	50	1	7
Cobalt	50	1	7
Copper	20	1	6
Iron	30	1	7
Lead	100	1	42
Magnesium	1		30
Manganese	10	0.2	2
Molybdenum	100	1	8
Nickel	40	1	15
Potassium	10		(see [3])
Selenium		2	75
Silica (SiO_2)			58
Silver	10	0.2	7
Sodium	2		29
Thallium	100	1	40
Vanadium	200	4	8
Zinc	5	0.05	2

[1] "Method for Chemical Analysis of Water and Wastes," EPA-600/4-79-020.
[2] The estimated instrumental detection limits as shown are taken from "Inductively Coupled Plasma-Atomic Emission Spectroscopy-Prominent Lines," EPA 600/4-79-017. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.
[3] Highly dependent on operating conditions and plasma position.

The need for lower limits of detection both in wastewater as well as in drinking water analyses subsequently resulted in EPA approval of the graphite furnace technique. A recently completed ASTM graphite furnace round-robin should result in inclusion of that technique in many of the metal standards for 1983.

Originally, 26 elements amenable to atomic absorption spectrometry were included in the wastewater monitoring program. While it was necessary for the regulating agencies to monitor for all 26 elements, dischargers frequently were required to report on a much smaller number. Consequently, atomic absorption instrumentation flourished. Rationale for approval of NIPDWR methodology followed similar criteria. For drinking water, however, only eight metals are regulated by the NIPDWR.

As the sample load increased and more analyses were required in monitoring programs, AA has suffered somewhat from its inability to measure more than a single metal at a time. With the introduction of Inductively Coupled Plasma (ICP) instrumentation there has been a renewed interest in multi-element emission spectroscopy. The types of ICP instrumentation currently available employ either a simultaneous or a sequential detection system.

A simultaneous system provides for more rapid analysis and would be preferred when the number of elements to be

Much of the recent research and analytical methodology for the Environmental Protection Agency (EPA) studies on trace elements was developed at the Andrew W. Breidenbach Environmental Research Center in Cincinnati, OH.

analyzed exceeds ten and the number of samples per day exceeds 50. The sequential system, on the other hand, is usually of less initial cost and offers greater flexibility in wavelength selection. This feature is most desirable when a spectral interference from the sample matrix is encountered. The interference can often be eliminated by choosing an alternate wavelength. When spectral interference is encountered with a simultaneous system, a separate channel must be available so that a correction factor from the interferent may be applied. Fortunately, there are few severe interferences and most are well documented. With this information and knowledge of the types of samples to be analyzed, an instrument can be custom-made to specific needs.

A most convincing argument for the utilization of ICP in water and waste analyses is its relative freedom from chemical interference. Additionally, the sensitivity is similar to flame AA; its precision is generally uniform over a concentration range of four orders of magnitude. To achieve a similar analytical working range with AA, dilution is often required. With ICP it is possible to measure the concentration of over 25 elements in a single analysis. In fact, the number of elements that can be measured is restricted more by the sample solubilization procedure used than by instrument design or the energetics of the technique. Table 2 provides a comparison of estimated instrumental detection limits for atomic absorption versus inductively coupled argon plasma spectrometry.

As interest for approval of this analytical technique for wastewater as well as drinking water increased, an EPA Users Group was formed to arrive at a standardized procedure for the successful application of ICP analyses to aqueous samples. The result of their endeavor is available as a published procedure entitled Method 200.7, Inductively Coupled Plasma-Atomic Emission Spectrometric Method for Trace Element Analyses of Water and Wastes. Sample preparation, recommended wavelengths, and required quality control procedures are included along with a discussion on possible interferences and tests for their identification and suggested corrective action when required. Because of the differences between various makes and models of satisfactory instruments, detailed operating instructions are not provided. This method is currently awaiting formal approval in the *Federal Register* for NPDES monitoring. In the interim, in as much as sufficient comparability data on wastewater are on agency file, requests for limited-use approval may be made through the regional administrator without additional test data. Interest in approval for drinking water analysis is also increasing. At this time, however, requests for limited-use do require analytical test data that demonstrate comparability with a currently approved test method. A proposed ICP test method was first published in March 1980, in Part 31, of the *Annual Book of ASTM Standards* and a collaborative test is being planned currently. ■

John F. Kopp, chief of the Physical and Chemical Methods Branch, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency (EPA), Cincinnati, OH, is a member of D-19 on Water and E-2 on Emission Spectroscopy. He is currently a task group chairman for the nickel, manganese and graphite furnace working groups of D-19.

Kopp received a B.S. and an M.S. in chemistry from Xavier University, and has been employed by the federal government for the past 35 years. He has been a member of ASTM for 12 years.

Theodore D. Martin, a research chemist in the same Branch of the EPA, has more than 20 years experience in trace element analysis by atomic emission and absorption spectroscopy. He is a member in the Society for Applied Spectroscopy, served on various subcommittees and participated in ASTM and International Organization for Standardization (ISO) round robin studies. Martin received a B.A. in chemistry from Earlham College.